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BY

STANLEY WARREN GLASS

B. S. (Kalamazoo College) 1922
A. M. (Harvard University) 1924

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE DEPARTMENT OF BROWN UNIVERSITY, 1926

[Reprinted from Jour. Amer. Chem. Soc., 47, 2892 (1925).]

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OXIDATION POTENTIALS AND EQUILIBRIA IN THE SYSTEM: CHLORINE, IODINE, HYDROCHLORIC ACID, WATER

For over a century the iodine chlorides have been extensively investigated. Sullivan's paper[1] was the first to deal with actual oxidation potentials. He opposed to calomel electrode a platinum electrode in iodine monochloride half normal in hydrochloric acid (which is much too dilute to suppress hydrolysis) with and without rubidium chloride. Five measurements of e.m.f. were made indicating (incorrectly) a process involving unit change of valence. Electrolysis with a parchment membrane gave iodine at the cathode (inevitably, as chlorine is the first to be reduced to its ion). An iodine electrode in monochloride differed from one in potassium iodide. Abegg[2] attributes the above results to the hypothetical ion, I^+, and states that the reversible potential of the process $I_2 \rightleftarrows 2I^+$ can be calculated from such data. These issues invite further investigation.

Willard and Fenwick[3] tried the method on manganic chloride, and state that the reaction had a good end-point, but that it did not proceed regularly except under carefully controlled conditions.

Kolthoff[4] records two electrometric titrations of iodide with iodate in hydrochloric acid about 2 *N*. Two papers by Müller and Junck[5] discuss the electrometric titration against the normal calomel electrode, of iodate, periodate and chlorine water with iodide ion in hydrochloric acid and in sulfuric acid. In hydrochloric acid 0.16 *N* to 0.4 *N* their titration curves bent sharply when very nearly two molecular equivalents of iodide had been added to one of iodate, but in 0.8 *N* acid 1.66 molecular equivalents and in 1.6 *N* acid 1.88 were used. Unhindered escape of chlorine must have caused error, as they point out. I always required exactly two molecular equivalents. As their acids were quite dilute, being in only one titration more than 0.8 *N*, much iodate was present, of which they take account. I was able to neglect hydrolysis, as my constants were independent of acid concentrations. Müller and Junck did not calculate concentration relations, molal potentials or equilibria from their results, and owing to the differences in conditions it is impossible to correlate my data with theirs. They discuss a number of reactions as possible explanations of their curves. It should be noted that they

[1] Sullivan, *Z. physik. Chem.*, **28**, 523 (1899).

[2] Abegg, "Handbuch der anorganischen Chemie," Hirzel, Leipzig, **1913**, IV², p. 472.

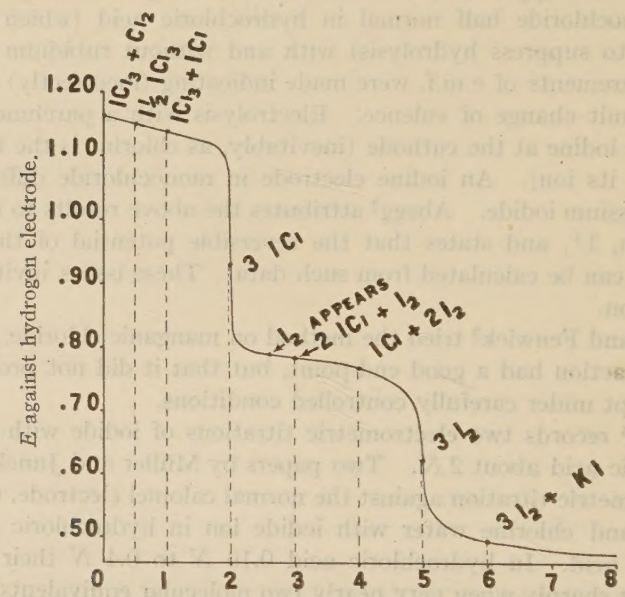
[3] Willard and Fenwick, *J. Am. Chem. Soc.*, **45**, 624 (1923).

[4] Kolthoff, *Rec. trav. chim.*, **39**, 212 (1920).

[5] Müller and Junck, *Z. Elektrochem.*, **31**, 200, 206 (1925).

predict $E=A + (0.058/4) \log C_{IO_3^-} C_{Cl^-} C^8_{H^+}/C_{ICl}$ which gives, upon the basis of a different mechanism, the slope which I found experimentally, for the unit chlorine-iodine ratio. Between the ratios unity and zero, they predict $E = A + (0.058/2) \log C_{ICl}/C_{I_2}C^2_{Cl^-}$ with which my equation is consistent.

Fig. 1, for orientation, gives a typical electrometric titration curve in a closed vessel, built up from several of the experiments. Iodide solution is added from a buret to 0.55 *M* iodate in 6 *N* hydrochloric acid,



Molecular equivalents of iodide added per equivalent of iodate.

Fig. 1.—Electrometric titration of iodate in hydrochloric acid.

and the e.m.f. corrected to constant volume by the equation $E_1 = E + 0.0297 \log (V/V_1)$. Beyond the point so indicated the solution is in equilibrium with precipitated iodine.

I have measured against hydrogen electrodes, in hydrochloric acid of three concentrations, oxidation potentials for chlorine and for chlorine plus iodine near the ratios 5, 3 and 1, all over considerable concentration ranges. I have generalized the data as linear equations and have calculated by extrapolation the molal potentials. Certain novel numerical relationships have been brought to light and explained fully.

Constant-boiling hydrochloric acid was prepared by diluting colorless, commercial 12 *N* acid with somewhat less than its volume of water and distilling from an all-glass apparatus. Portions of the distillate were suitably diluted and all were kept in Non-sol bottles. When this acid was analyzed against gently ignited sodium carbonate, with the usual precautions, the normalities found were 6.078, 4.979 and 4.000.

The hydrogen electrodes, of conventional type, carried frequently replatinized platinum electrodes 1 sq. cm. in area. Sodium hydroxide was electrolyzed between nickel cathodes and platinum anodes. The hydrogen was dried, passed over hot copper, and then through three bottles of acid of the same concentration as that in both electrodes, the last bottle being in the thermostat. Every few days all of the acid in the train was replenished. Stringent precautions were taken against the presence of oxygen during measurements. Two (and often three) hydrogen electrodes were operated together, checking in almost all cases within 0.00005 volt. Readings were reduced to 760 mm. partial pressure of hydrogen by correction for barometer, for depth of immersion of electrodes, and for total vapor pressure of the acids based on Zeisberg's collected data.[6] $\Delta E/p_{HCl} = 0.000017$ volt/mm., and p_{HCl} was 18.1, 16.3 and 14.5 for 4, 5 and 6 N acid, respectively. The bridge was a large beaker of 4, 5 or 6 N acid. There were no junction potentials, of course. No attempt was made to correlate data with normal hydrogen electrode.

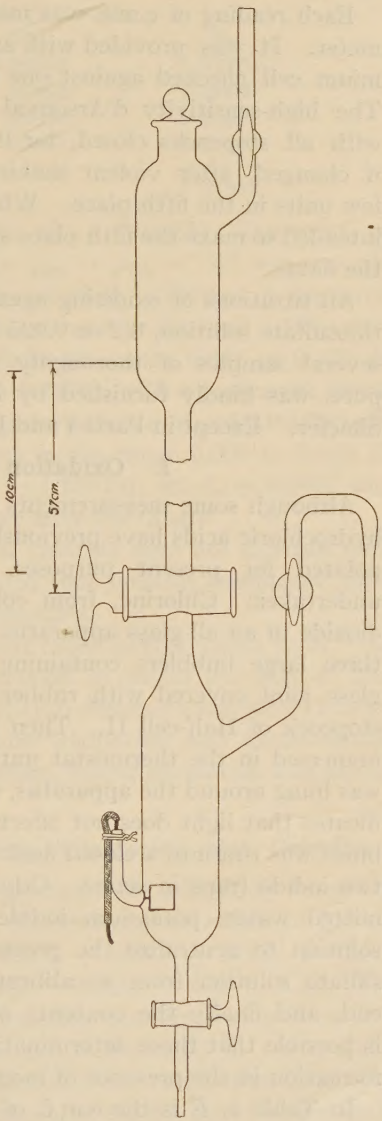


Fig. 2.—Iodine chloride cell.

Half-cell I, for halogens appears in Fig. 2. A calibrated buret is set between two bulbs of 125cc. capacity, the lower one having a platinum-iridium electrode 1.5 sq. cm. in area. The lowest stopcock was immersed in the bridge solution for the brief periods of measurement. Half-cell II was similar, but lacked the large stopcock above the lower bulb, also the upward bend of the side arm, whose descending portion dipped into the bridge solution.

The chain was kept at 25.00 ±0.02° international scale in a large kerosene thermostat, the thermostat thermometer being referred to Reichsanstalt thermometer No. 42,547, whose

[6] Zeisberg, *Chem. Met. Eng.*, **32**, 326 (1925).

ice-point had been recently checked. If the temperature of the entire chain varied, $\Delta E/\Delta T = -0.0007$; if only that of Half-cell I or II varied, $\Delta E/\Delta T = -0.0001$ for the chain.

Each reading of e.m.f. was made on a very accurate Wolff potentiometer. It was provided with an equipotential shield and a standard cadmium cell checked against one certified by the Bureau of Standards. The high-sensitivity d'Arsonval galvanometer gave positive deflections, with all stopcocks closed, for 0.00001 volt. No reading was accepted if changed, after violent shaking of Half-cell I or II, by more than a few units in the fifth place. While the precautions and corrections were intended to make the fifth place significant, it is not retained in presenting the data.

All titrations of oxidizing agents were made by iodimetry. Well-aged thiosulfate solution, 0.2 or 0.025 *N*, kept in the dark, was compared with several samples of thoroughly dried iodine. One of these, extremely pure, was kindly furnished by Professor G. P. Baxter and Mr. W. E. Shaefer. Except in Parts I and II, a weight buret was used.

I. Oxidation Potential of Chlorine

Although some measurements of this potential[7] in rather concentrated hydrochloric acids have previously been made, none could safely be interpolated for present purposes. Therefore, new determinations were undertaken. Chlorine, from colorless commercial acid and manganese dioxide in an all-glass apparatus, passed through glass wool and through three large bubblers containing dilute acid. Through an overlapping glass joint covered with rubber, chlorine passed up through the lower stopcock of Half-cell II. Then the half-cell was alternately shaken and immersed in the thermostat until the e.m.f. was constant. Black cloth was hung around the apparatus, although a preponderance of evidence indicates that light does not affect this e.m.f. A portion measured on the buret was run into a closed flask full of carbon dioxide and provided with two iodide traps in series. Other tubes passing through the stopper admitted water, potassium iodide solution in excess, sodium hydroxide solution to neutralize the greater part of the acid, and standard thiosulfate solution from a calibrated buret. Starch was added near the end, and finally the contents of the iodide traps were washed in. It is possible that these determinations were slightly affected by perchlorate formation in the presence of momentary local excess of alkali.[8]

In Table I, E is the e.m.f. of chlorine in 6.078 *N* acid at 25.00° with corrections for hydrogen electrode [Cl_2], the concentration of chlorine in

[7] Dolezalek, *Z. physik. Chem.*, **26**, 321 (1898). Foerster, Nobis and Stötzer, *Z. Elektrochem.*, **29**, 64 (1923), citing also data by E. Noack, otherwise unpublished.

[8] Philipp, *Ber.*, **3**, 4 (1870). See also Philip and Bramley, *J. Chem. Soc.*, **107**, 379 (1915).

moles per liter by titration and E_0 the molal potential from the formula $E_0 = E - 0.02972 \log [Cl_2]$.

TABLE I

MOLAL POTENTIAL OF CHLORINE

Solution	E	$[Cl_2]$	E_0
a	1.14777	0.00597	1.21388
b	1.15951	.01492	1.21380
c	1.17405	.04633	1.21371
d	1.18403	.09905	1.21389
			1.21382

Equation 1 follows, $\log [Cl_2] = 33.64 (E - 1.2138)$. The e.m.f. of the cell $H_2 \mid 6.078\ N$ HCl $\mid Cl_2$, where $p_{H_2} = p_{Cl_2} = 760$ mm., would follow, given $[Cl_2]$ in the corresponding solution. Solution d appeared to be nearly saturated, indicating that E_{760} cannot be far from 1.185 volts.

In 4.979 N acid my four experiments in the range 0.041 to 0.167 M gave Equation 2, $\log [Cl_2] = 33.64 (E - 1.2478)$, with a maximum deviation, m. d., of 0.00037 volt and an average deviation, a. d., of 0.00025 volt.

In 4.000 N acid my seven experiments in the range 0.006 to 0.160 M gave Equation 3, $\log [Cl_2] = 33.64 (E - 1.28010)$; m. d. = 0.0025 and a. d. = 0.0009, one result diverging widely from the others.

As the extrapolated molal potential of chlorine does not increase with $[Cl_2]$ in any of the acids, it was concluded that possible complexes[9] such as $Cl_2.nCl'$ are equally unstable in all the acids.

Equations 1 to 3 have been used without evident error, down to $10^{-16}\ M$ to estimate $[Cl_2]$, that is, the concentration in moles per liter of free chlorine responsible for E. I shall use [Cl] to designate the total chlorine per liter present as free chlorine, iodine trichloride and monochloride and [I] as total iodine present as free iodine, iodine trichloride and monochloride.

II. Oxidation Potentials with Iodine Trichloride plus Chlorine

Potassium iodate, U. S. P., or highly purified iodic acid kindly furnished by Professor G. P. Baxter and Mr. W. E. Shaefer, was added to 200 cc. of acid previously run into Cell II. $KIO_3 + 6HCl = 3H_2O + Cl_2 + 6KCl + ICl_3$ (or $KICl_4$); $HIO_3 + 5HCl = 3H_2O + Cl_2 + ICl_3$. The hydrochloric acid to be oxidized in the reaction was supplied as described in Part III, to make the final normality 6.08, 4.98 or 4.00 N. After shaking the stoppered vessel, the excess of pressure due to chlorine formation was relieved. When the e.m.f. was constant, at 25.00°, after further shaking, total halogen remaining in solution was titrated as in Part I. Here, also, a small amount of perchlorate may have been formed. The known iodine concentration was subtracted to find the chlorine. Finally e.m.f.

[9] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899). Mellor, *J. Chem. Soc.*, **79**, 237 (1901).

was slightly extrapolated to correspond to $ICl_3 + Cl_2$ by adding 0.0297 log [I]/$^1/_4$([Cl]-[I]). As the corrected results, when graphed, indicate straight lines, Table II sufficiently represents them. It includes the "best" equation, concentration range of iodine in equivalents per liter, number of separate experiments, also maximum and average deviation in e.m.f. from the linear equation. E_0 is the e.m.f. extrapolated for a solution containing per liter exactly one equivalent of iodine and five of chlorine.

TABLE II

MOLAL POTENTIAL OF IODINE TRICHLORIDE PLUS CHLORINE

	N	Equation	E_0	Range	Expts.	M. d.	A. d.
(4)	6.079	0.0263 log [I] = E-1.2064		0.007–0.070	5	0.0008	0.0004
(5)	4.979	.0263 log [I] = E-1.2403		.005– .054	4	.0007	.0004
(6)	4.000	.0263 log [I] = E-1.2731		.007– .070	6	.0008	.0004

Potassium iodate and iodic acid unexpectedly yielded the same molal potential. In view of the probability of complex formation, it would seem more rational to add potassium iodate and six molecular equivalents of acid, thus forestalling undue elevation of e.m.f. through suppression of chloride ion belonging to the original acid.

III. Oxidation Potentials with Iodine Trichloride

For this part P. W. R. Analytical potassium iodate and iodide, carefully dried, were used. The iodate was twice analyzed and liberated 6.013 and 6.015 equivalents of iodine per formula weight. The iodide was next titrated electrometrically against it, combining in Cell I two formula weights of iodide to one of iodate. A small volume of very dilute standard iodide solution then completed the reaction. The iodide was found to be 99.56% and 99.76% pure, assuming that the iodate was 100.00% pure.

In each determination of oxidation potential, V cc. of acid 6.08, 4.98 or 4.00 N was mixed with (100-V) cc. of a stronger acid of known normality. The calculation provides for the disappearance of six molecular equivalents of acid per equivalent of iodate and for the formation of three equivalents of water. In some cases, where the amount of stronger acid actually added was not quite sufficient to yield a final solution 6.08, 5.98 or 4.00 N, small corrections were later applied to the e.m.f. These were based on special parallel experiments where the acid concentration in Half-cell I was the only variable; $\Delta E/\Delta N$ (average) = —0.0255. About 80 cc. of the mixed acid was first run into the electrode chamber through a funnel tube. The air was displaced by carbon dioxide and the funnel tube dried. Through it the dry salts were poured and the last traces washed in with the rest of the mixed acid. Upon promptly closing the large stopcock and shaking, a partial vacuum resulted,

so that no chlorine escaped from the chamber. The chlorine in the gas phase, uniformly 23.5 cc., was always estimated from analyses of known volumes of gas phases in equilibrium with similar solutions. As the salts were weighed out according to their formula weights, the actual reaction involved 0.9966 potassium iodide to 2.0000 potassium iodate, and (9 + 0.0034) equivalents of chlorine resulted. From this was subtracted the chlorine in the vapor phase, giving [Cl]. Finally, the e.m.f. was extrapolated to correspond to iodine trichloride by adding 0.0297 log $[I]/{}^1/_2([Cl]-[I])$, which never exceeded 0.0006 volt. The summary of data for a single typical experiment is given in Table III.

TABLE III

MOLAL POTENTIAL AND DISSOCIATION CONSTANT OF IODINE TRICHLORIDE

	Mole		
KIO_3, 0.3000 g.	0.0014016 KIO_3	log $[I]/{}^1/_2([Cl]-[I])$	0.00499
KI, 0.1164 g.	.0006987 KI	t, ° C.	25.00
98.7 cc. of 6.08 N HCl	.6001 HCl	E observed, volts	1.14005
1.3 cc. of 11.3 N HCl	.0147 HCl	Barometer	—0.00008
Total acid	.6148 HCl	Immersion	— .00002
Oxidized by KIO_3	.0084 HCl	Pressure, acid	+ .00025
Residual acid	.6064 HCl	0.0297 log $[I]/{}^1/_2([Cl]-[I])$	+ .00015
Water formed; 0.0042 mole	.08 cc.	.0255 ΔN	— .00053
Normality of acid	6.058	E corrected	1.1398
Required normality	6.079	E_0, 6.08 N HCl	1.2138
ΔN	—0.021	$(E-E_0)(33.64)$	—2.4894
KIO_3 produced	.006309 Cl	log $[Cl_2]$	3.5106
Vapor phase	.000056 Cl	$[Cl_2]$	0.00324
Residual chlorine	.006253 Cl	${}^1/_2([Cl]-2[Cl_2]-[I]) = [ICl_3]$	.0175
Total equivalents I	.002100 I	$[I]-[ICl_3] = [ICl]$	.0035
$[I]$	.02100	K	6.4×10^{-4}
$[I]/[Cl]$	.3358	Deviation from average	-0.8×10^{-4}

The corrected results, when graphed, indicate straight lines, and are sufficiently represented by Table IV. The captions are the same as for Table II except that E_0 is here the e.m.f. extrapolated for a solution containing per liter exactly one equivalent of iodine and three of chlorine.

TABLE IV

MOLAL POTENTIAL OF IODINE TRICHLORIDE

	N	Equation	E_0	Range	Expts.	M. d.	A. d.
(7)	6.079	0.0124 log $[I] = E$-1.1606		0.004–0.210	6	0.0020	0.0010
(8)	4.979	.0124 log $[I] = E$-1.1966		.035– .140	5	.0008	.0004
(9)	4.000	.0124 log $[I] = E$-1.2287		.070– .140	4	.0004	.0003

The unexpectedly small value of the slopes, which obtains only when $[Cl]/[I]$ is very nearly 3, is explained mathematically below.

To solve the equation $[ICl][Cl_2] = K[ICl_3]$ for K, we have $[Cl_2]$ from the e.m.f. and Equations 1 to 3. $[I]$ is calculated from the weights and composition of the salts. Then $([Cl]-2[Cl_2])$ = combined chlorine and $([Cl]-2[Cl_2]-[I])$ is chlorine free to combine with monochloride to form trichloride, whence $[ICl_3] = ([Cl]-2[Cl_2]-[I])/2$ and $[ICl]$ =

($[I]-[ICl_3]$). Six experiments in 6 N acid average 7.3×10^{-4}; five in 5 N acid, 7.0×10^{-4}; and four in 4 N acid average 7.3×10^{-4}; the average of all gives $K = 7.2 \times 10^{-4}$; m. d., 3.1×10^{-4}; a. d., 1.3×10^{-4}. Apparently the supposed complex ICl_4^- is very stable, for K is independent of $[Cl^-]$. Hydrolysis appears to be negligible, as K is independent of H^+.

An independent set of values for K with ICl in excess was next obtained, starting with monochloride obtained according to Berzelius[10] by distilling P. W. R. Analytical potassium chlorate and iodine, and redistilling from potassium chlorate. Samples of the liquid distillate, later found by three analyses to contain chlorine and iodine in the ratio 1.017 ± 0.003, were at once sealed in weighed tubes provided with capillary ends. A weighed sample was dissolved in a known volume of 6 N acid in Half-cell II, which was connected through a bridge to a special cathode compartment. Small, known amounts of current were then passed and the totals were graphically integrated from readings of an ammeter checked against an iodine coulometer. The quantities of chlorine produced at the anode in Half-cell II were then found, and the values of total chlorine calculated. From the series of readings of e.m.f., free Cl_2 was calculated for each case; [I] was known from the weight and composition of the monochloride taken. Consequently, K could be calculated as described above. Eight experiments gave $K = 8.4 \times 10^{-4}$; maximum deviation, 0.5×10^{-4}; minimum deviation, 0.4×10^{-4}.

IV. Oxidation Potentials with Iodine Monochloride

This problem was first attacked by measuring, in the various acids, the e.m.f. of samples of the liquid monochloride just described. But these results could not be correlated with concentration, and it soon appeared that so near unit value of the ratio [Cl]/[I], minute variations in composition gave rise to very large differences in e.m.f. The desired values were, therefore, found indirectly. Potassium iodate and iodide (described in Part III) were weighed out according to the equation $KIO_3 + 2KI + 6HCl = 3H_2O + 3KCl + 3ICl$ (or $3KICl_2$). Acid was made up, with compensation as previously described for acid to be oxidized by iodate, except that the water formed was not considered because the mixture was made up to 100 cc. in a flask. No correction for chlorine in the gas phase was needed. The initial mixtures corresponded to the ratio [Cl]/[I] = 1.0046. Dil. potassium iodide solution 0.012 M dissolved in the proper acid was then added from a buret, drop by drop, through the top of Half-cells I and II. This was shaken to constant e.m.f. at 25.00° and the added iodide calculated. This process was repeated on the aver-

[10] Berzelius, see Gmelin-Kraut, "Handbuch der anorganischen Chemie," Carl Winter, Heidelberg, **1909**, vol. 1, pt. 2, p. 395. Thorpe, *J. Chem. Soc.*, **37**, 175 (1880).

age fourteen times in each of eighteen sets of experiments, a special effort being always made to get one case close to the unit ratio where e.m.f. was changing rapidly. Owing to polarization such values were very unstable, and could not be interpolated to the true ICl point. After the usual corrections for hydrogen electrode and for any slight irregularity in acid concentration, the e.m.f. was referred to 100 cc. by $E_{100} = E_V + 0.0297 \log (V/100)$, which was proved applicable by graphical treatment of three complete sets of experiments. The value of $[Cl_2]$ resulted in each case from E and Equations 1 to 3. As $ICl + I^- = I_2 + Cl^-$, $[I_2]$ = the moles of iodide added after passing the mid-point of the steep portion of the electrometric titration curve; [ICl] = moles of iodine monochloride at the mid-point minus moles of iodide added beyond that point. The equation $[I_2]\,[Cl_2] = K_1[ICl]^2$ was now solved for K_1, using only data far enough from the mid-point to insure steadiness of e.m.f. The summary of data for a single typical experiment is given in Table V. Fifty-eight calculations of K_1 made from eighteen sets of experiments

TABLE V

MOLAL POTENTIAL AND DISSOCIATION CONSTANT OF IODINE MONOCHLORIDE, ICl

	Mole		
KIO_3, 1.0000 g.	0.004672 KIO_3	t, ° C.	25.00
KI, 1.5540 g.	.009328 KI	E observed, volts	0.85924
3.7 cc. of 11.3 N HCl	.0418 HCl	Barometer, volts	+ .00007
96.3 cc of 4.98 N HCl	.4795 HCl	Immersion, volts	− .00002
14.95 cc. of 4.98 N HCl	.0745 HCl	Pressure HCl, volts	+ .00028
Total acid	.5958 HCl	0.0297 log (114.95/100), volts	+ .00179
Oxidized by KIO_3	.0280 HCl	.0255 ΔN, volts	− .00101
Residual acid	.5678 HCl	E corrected, volts	.86026
Total volume	114.95 cc.	E_0	1.2478
Normality	4.939	$(E - E_0)(33.64)$	−13.035
Required normality	4.979	log $[Cl_2]$	$1\bar{4}.964$
ΔN	−0.040	$[Cl_2]$	9.2×10^{-14}
KI, 14.95 cc. of 0.0122 M	.000179 KI	$\frac{1}{2}([I] - [Cl]) = [I_2]$	1.16×10^{-3}
Total Cl per liter after end-point	.12102	$[ICl] = [Cl]$	1.21×10^{-1}
Total I per liter after end-point	.12335	K	7.3×10^{-15}
Ratio [Cl]/[I]	.9811	Deviation from av. =	-0.5×10^{-15}

in three acids average 7.8×10^{-15}; m. d., 2.0×10^{-15}; a. d., 0.8×10^{-15}. The percentage error is large because the *first* significant figure of each constant comes from the *third* significant figure of a logarithm. There was no variation attributable to changing acid concentration, so apparently the stability of $ICl.nCl'$ is as great in 4 N as in 6 N acid and hydrolysis is negligible.

An attempt was made to interpolate the e.m.f. corresponding to exactly unit value of the chlorine-iodine ratio by assuming that at this point $[I_2]_1 = [Cl_2]_1 = \sqrt{K_1[ICl]^2}$ and that $E_1 = E_0 + 0.0297 \log \sqrt{K_1[ICl]^2}$. But in each case E_1 lay near the top of the steep portion of the electrometric titration curves especially when [ICl] was large.

Correction was, therefore, made for iodine trichloride formation. $K_1/K = [I_2]\,[ICl_3]/[ICl]^3 = K_3 = 1.1 \times 10^{-11}$. Close to the unit ratio point [ICl] is practically constant for large changes in E and is practically equal to [I]. Then $[ICl_3] = [ICl]\,[Cl_2]/K = b[Cl_2]$ where b is $[ICl]/K$ and is constant for given [ICl]. From this and the condition that [I] = [Cl], $[I_2] = (b + 1)\,[Cl_2]$. When [ICl] approaches zero, b approaches zero, and $[I_2] = [Cl_2]$; but when [ICl] = 0.16, $[I_2] = 230[Cl_2]$. Substituting $[Cl_2]$, $b[Cl_2]$ and $(b + 1)\,[Cl_2]$ in the equation for K_1, $[Cl_2] = \sqrt{K_1[ICl]^2/(b + 1)}$ at the unit ratio point, and at the same point $E = E_0 + 0.02972 \log \sqrt{K_1[ICl]^2/(b + 1)}$.

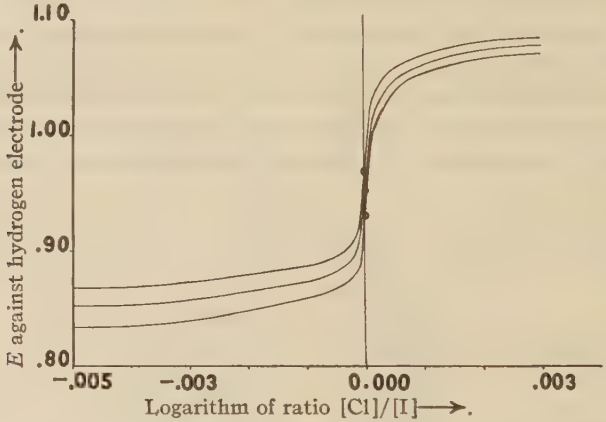


Fig. 3.—Electrometric titrations through iodine monochloride point. Top point, [I] = 0.1353; middle point, [I] = 0.0333; bottom point, [I] = 0.0093.

These calculated values for E all lie halfway down the rapidly descending portions of curves like those shown in Fig. 3, where they are indicated by circles. These values would be obtained directly with samples of monochloride so pure that neither halogen was in excess by more, perhaps, than one millionth of one per cent.

E as calculated was now plotted against [ICl], and the linear equations found.

TABLE VI

MOLAL POTENTIAL OF IODINE MONOCHLORIDE

	N	Equation	E_0	Range	M. d.	A. d.
(10)	6.079	0.0154 log [ICl] = (E-0.9572)		0.004–0.163	none	none
(11)	4.979	.0154 log [ICl] = (E- .9912)		.004– .135	none	none
(12)	4.000	.0154 log [ICl] = (E-1.0235)		.004– .137	none	none

Because K and K_1 are both independent of acid concentration the three slopes must be identical, and because E is calculated from them, deviations are impossible. These slopes, like those for trichloride, at first sight indicate an oxidation-reduction process involving a valence change of *four*,

and it is evident that Sullivan erred greatly in reporting the apparent valence change as unity. It is readily shown, however, that the slopes are not inconsistent with the assumption that the only electrochemical process is $Cl_2 + 2\ominus \rightleftarrows 2Cl'$. For since $[Cl_2] = \sqrt{K_1[ICl]^2/(b+1)}$, where $b = [ICl]/K$, we have $\log [Cl_2] = \log ([ICl]\sqrt{KK_1}) - \log\sqrt{[ICl]+K}$. Also $\log [Cl_2] = 33.64\ (E-E_0)$. Then by substitution and differentiation, $d \log [ICl] - {}^1/_2\ d \log ([ICl] + K) = 33.64\ dE$. Expanding and uniting terms, and noting that K is small compared with [ICl], $d[ICl]/2[ICl] = {}^1/_2\ d \log [ICl] = 33.64\ dE$, or finally, $dE/d \log [ICl] = 0.0149$ when [Cl]/[I] = 1 (exactly). Further treatment of these equations shows that the slopes increase very rapidly on either side of this "end-point," soon approaching the value 0.0297 required by the process $Cl_2 + 2\ominus \rightleftarrows 2Cl'$.

The slope $\Delta E/\Delta \log [ICl_3] = 0.0124$, experimentally determined for absolutely pure iodine trichloride, also simulates a valence change of *four*, and can also be predicted mathematically. From $[ICl]\,[Cl_2] = K[ICl_3]$ it follows that $[ICl] = K[ICl_3]/[Cl_2]$ or $[ICl] = Ky/c$, where y is taken as a variable. When [Cl]/[I] is exactly three, the chlorine present as free chlorine and iodine monochloride must equal three times the iodine present as monochloride and free iodine. Then total chlorine, excluding that present as trichloride, equals $2c + Ky/c$ or $(2c^2 + Ky)/c$. The corresponding iodine is then $(2c^2 + Ky)/3c$, of which Ky/c is ICl. In consequence, $[I_2] = (c^2 - Ky)/3c$. Substituting in the equation $[I_2]\,[ICl_3] = K_3\,[ICl]^3$, and solving for c in terms of y, we obtain $[Cl_2] = \sqrt{[ICl_3](K/2 + \sqrt{K^2/4 + 3K_3K^3})}$. Then $\log [Cl_2] = \log \sqrt{[ICl_3]} + \log \sqrt{K/2 + \sqrt{K^2/4 + 3K_3K^3}}$. But $\log [Cl_2] = 33.64\ (E - E_0)$; hence, $d \log [ICl_3]/2 = 33.64\ dE$ and the slope $dE/d \log [ICl_3] = 0.0149$, in fair agreement with the observed slope 0.0124. Further treatment shows that this slope increases rapidly on either side of the exact ICl_3 point, soon approaching the value 0.0297. The plot of E against log ([Cl]/[I]) must have an inflection at the ICl_3 point, but this question was not investigated experimentally.

V. Oxidation Potentials for Minimal Ratios of Iodine Chloride to Iodine

Except for the purposes of Fig. 1, systems for which the chlorine-iodine ratios were less than 0.73, were not investigated. Except in very dilute iodine monochloride solutions, iodine is precipitated when the ratio is made much smaller. It was found that the solubility of iodine in 6 N acid at 25°, though greater than in water, is only 0.028 equivalent per liter. Theoretically, every e.m.f. along the curve in Fig. 1 could be treated as a chlorine potential. To the right of the point designated $3I_2$, poly-iodide ions complicate the situation. The steeply ascending

portion just to the left of the same point could be used practically to estimate roughly the percentage, in samples of iodine, of impurities of higher oxidizing potential.

VI. The Hypothetical Ion I^+

My data are fully accounted for by attributing each e.m.f. observed to the chlorine molecule. This could not be done in terms of the ion I^+. In particular we should have to write for the monochloride, $E = E_0 + 0.06 \log [I^+]$, whereas the slope was found to be only one-fourth as great. Also, no sudden change in $[I^+]$, at the point where [Cl] = [I], could be predicted from the above equation and $[I^+] = k[ICl]/[Cl']$. I have not proved that the ion I^+ does not exist in aqueous solutions, but I have proved invalid the strongest argument hitherto urged in its behalf.

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Summary

Oxidation potentials at 25.00° for chlorine, for iodine trichloride plus chlorine, for iodine trichloride and for iodine monochloride have been measured in hydrochloric acid 4, 5 and 6 N against hydrogen electrode in the corresponding acids, throughout a wide range of concentration, and expressed by linear equations. These contain the extrapolated "normal" (molal) potentials.

If escape of chlorine is avoided and platinum-iridium electrodes are used, the above-mentioned systems can be titrated electrometrically with great accuracy.

The constant K for $[ICl]\,[Cl_2] = K\,[ICl_3]$ is 7.2×10^{-4}; K_1 for $[I_2]\,[Cl_2] = K_1\,[ICl]^2$ is 7.8×10^{-15}; K_3 for $[I_2]\,[ICl_3] = K_3\,[ICl]^3$ is 1.1×10^{-11}. All these constants are independent of acid concentration within our limit of error.

The molal potential E_0 of iodine monochloride, being excessively sensitive to the smallest change in chlorine-iodine ratio, was found indirectly with the help of K_1. The solution contains more free iodine than free chlorine.

Two cases were discovered where the slope $\Delta E/\Delta \log c$ indicates a valence change twice as great as that actually occurring. For *pure* iodine trichloride, $E = E_0 + 0.0124 \log [ICl_3]$ and for *pure* iodine monochloride

$E = E_0 + 0.0154 \log [ICl]$ in each acid concentration. This peculiar relation is also predicted mathematically.

All relations among data can be fully explained on the basis $Cl_2 + 2\ominus \rightleftarrows 2Cl'$, and scarcely any on the basis $ICl \rightleftarrows I^+ + Cl'$.

A very sensitive method for testing iodine for impurities having higher oxidation potentials is suggested.